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For: RUST-RESISTANT CALCIUM STEEL

Also enclosed are:

- ☒ Petition to Accept Photographs, 4 Sheets of drawings, Fig. 1 in triplicate, and \$130.00 Check
- ☒ Recordation Form Cover Sheet - Patents Only and an Assignment of the invention to Kawasaki Steel Corporation
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RUST-RESISTANT CALCIUM STEEL

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to a Ca-containing  
rust-resistant steel, containing Ca at a concentration of  
about 5 ppm or more. In particular, it relates to the  
concept of effectively reducing the formation of rust on  
surfaces of steel products, such rust being caused by CaO-  
containing oxide inclusions in the steel products, thereby  
10 solving a problem which is often of concern when Ca or Ca  
alloy is added to molten steel.

In accordance with this invention, the formation of  
large cluster-like inclusions, which would otherwise  
result due to the low melting point of the oxide  
15 inclusions, is prevented.

This invention further prevents nozzle clogging  
during the associated continuous casting process, and  
reduces deformability during hot rolling of sulfide  
20 inclusions.

Description of the Related Art

25 There has long been a demand for common steels such  
as low carbon steels and extremely low carbon steels, as  
well as for various stainless steels, particularly thin  
steel sheets, to achieve esthetically pleasing exterior  
surface appearances. These steel products can usually be  
processed into low carbon steels by deoxidation treatments  
using Al, Ti, or Si to combine with oxygen in the steel.

However, it is still impossible to avoid the formation of deleterious amounts of oxide inclusions in the steel products treated by Al-deoxidation or Ti-deoxidation. In fact, the oxide inclusions usually contain as their main components  $\text{Al}_2\text{O}_3$  and Ti oxide, each in an amount corresponding to an oxygen content of 10 to 80 ppm.

The above oxide inclusions, mainly containing  $\text{Al}_2\text{O}_3$  and Ti oxide, are likely to adhere to and thus form deposits on the internal surfaces of an immersion nozzle of the type usually employed in a continuous casting process for injecting molten steel from a tundish into a mold. As a result, the nozzle is likely to clog, making it impossible to ensure the performance of a stable casting process.

Moreover, flakes of deposited materials tend to come off the nozzle and mix into the steel product, resulting in defects in the physical properties of the steel product. Furthermore, due to the clogging of the continuous casting nozzle, the flow of the molten steel becomes deflected within the casting mold, thus resulting in the problem in that particles on the surface of the molten metal within the casting mold will be undesirably mixed into the molten metal. In addition, since  $\text{Al}_2\text{O}_3$  and Ti oxide tend to form cluster-like inclusions, which usually remain on the surface of a thin steel sheet,

striped defects form on the surface of the steel sheet,  
making it difficult to achieve a good external appearance.

In order to overcome these problems caused by  $\text{Al}_2\text{O}_3$   
and Ti oxide, it has been suggested to add Ca to molten  
5 steel treated by Al-deoxidation, to form an oxide  
composition consisting of CaO and  $\text{Al}_2\text{O}_3$ . Such methods are  
disclosed in, for example, Japanese Unexamined Patent  
Application Publication Nos. 61-276756, 58-154447, 6-  
49523).

10 However, it has been found that if Ca is added and is  
caused to react with  $\text{Al}_2\text{O}_3$ , some oxides having low melting  
points also form. These low melting oxides contain  $\text{CaO} \cdot$   
 $\text{Al}_2\text{O}_3$ ,  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  as their main  
components.

15 However, problems arise in MnS steels, including HIC  
resistant steels, and in steels required to possess a  
desired burring characteristic, and other steels  
containing MnS. Since the MnS contained in the steel  
tends to assert harmful influences on the desired HIC  
20 resistance and burring properties of the steel, it has  
also been suggested that Ca be added in order to inhibit  
the formation of MnS (For example, Japanese Unexamined  
Patent Application Publication No. 56-9317).

25 However, whenever Ca is added to a molten steel, the  
added Ca also reacts with the S contained in the steel,

undesirably forming CaS, which causes the subsequent formation of rust on the surfaces of the steel products.

In an attempt to solve these complicated problems, Japanese Unexamined Patent Application Publication No. 6-559 has suggested that the Ca content of a steel product be controlled within a range of 5 ppm to less than 10 ppm, so as to prevent the formation of rust on the surface of the steel product. However, even though the Ca content is controlled to a value which is less than 10 ppm, if the composition of the oxides remaining in the steel is not specifically controlled, and if the CaO concentration in a resulting inclusion is high, the problem remains that CaS cannot be prevented from forming in the areas around the CaO-containing oxides that remain in the steel, hence forming numerous starting points at which rust will subsequently develop.

As a result, the time period before rust forms on the surface of a steel product (after the steel product has been produced) is undesirably shortened, thus increasing the amount and speed of rust formation, rendering it impossible to avoid deterioration of the external appearance of the steel products.

#### SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to prevent nozzle clogging, to render Al and Ti oxides

harmless, and to control the formation of sulfides, so as to produce an improved Ca-containing steel that is resistant to formation of the rust that is otherwise caused by inclusions formed on the steel surface.

5           As a result of extensive research, we have found that not every CaO-containing oxide inclusion causes formation of CaS in areas surrounding the oxide inclusions, nor will they all become the starting points for subsequent rust formation.

10           We have discovered that certain compositions of oxide inclusions actually create a situation in which the solubility of S in the oxides is decreased. We have further discovered that a solidification process conducted at a low temperature, as defined hereinafter, does not cause significant formation of CaS in areas around the oxide inclusions, whereby the oxides on the steel surface do not become effective starting points for future rust formation.

15           According to the present invention, we have provided an improved Ca-containing rust-resistant steel, wherein the composition of any oxide inclusions and the concentration of S contained in the steel are controlled so that among CaO-containing oxide inclusions about 80% of the oxide inclusions having particle diameters of at least  
20           2  $\mu$ m have an equilibrium S soluble amount (%S inc.) (to be  
25

further defined) which is about 0.03 wt% or less.

Furthermore, according to the present invention, it is preferred to use an equilibrium S-soluble amount (%S inc.), determined in accordance with the following equation (1), including as parameters the optical basicity based upon the composition of the oxide inclusions, the casting temperature, and components forming the steel product, wherein:

$$\begin{aligned} \log (\%S \text{ inc.}) &= (21920 - 54640\Lambda)/T \\ &+ 43.6\Lambda - 23.9 - \log [aO] + \log [\text{wt}\%S] \quad \dots (1) \end{aligned}$$

wherein

T represents the casting temperature (K) during the continuous casting process,

[wt%S] represents the concentration by weight of S in the steel,

[aO] represents the oxygen activity of the molten steel at the casting temperature (T) during the continuous casting process, and wherein, during Al-deoxidation of the steel,

$$\begin{aligned} \log aO &= (-64000/T + 20.57 - 2\log[\text{wt}\%Al] - \\ &0.086[\text{wt}\%Al] - 0.102 [\text{wt}\%Si]/3, \end{aligned}$$

and wherein, during Ti-deoxidation of the steel,

$$\begin{aligned} \log aO &= (-60709/T + 20.97 - 2\log[\text{wt}\%Ti] - \\ &0.084[\text{wt}\%Ti]/3, \end{aligned}$$

and provided that, when Al and Ti are present in the



steel, a smaller  $a_O$  oxygen activity is provided, wherein

$\Lambda$  represents optical basicity of oxide inclusions according to the following equation (2):

$$\begin{aligned} \Lambda = & 1.0 X(\text{CaO}) + 0.605 X(\text{Al}_2\text{O}_3) + 0.601 X(\text{TiO}_2) \\ & + 0.78 X(\text{MgO}) + 0.48 X(\text{SiO}_2) + 0.55 X(\text{Cr}_2\text{O}_3) \\ & + 0.59 X(\text{MnO}), \quad \dots (2) \end{aligned}$$

and wherein  $X(\text{MmOn})$  represents the cation equivalent of the oxide present, according to the following equation (3):

$$X(\text{MmOn}) = n \times N(\text{MmOn}) / \sum (n \times N(\text{MmOn})) \quad \dots (3)$$

and wherein  $N(\text{MmOn})$  represents the mol fraction of oxide present and

$n$  represents the valence of the oxygen contained in said oxide.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows EPMA measurement results of inclusions contained in steel blocks, representing both an example of the present invention and a comparative example.

Fig. 2 is a graph showing the relationship between

(a) the equilibrium S soluble amount (%S inc.) of oxides at a certain casting temperature and

(b) the rust formation developed in areas around the oxides during rust formation testing. This was prepared using an experimental apparatus containing a chamber having a constant temperature of 60°C and a constant

humidity of 95%.

Fig. 3 is a graph indicating the relationship between  
(a) the equilibrium S soluble amount (%S inc.) of  
oxides at a specific casting temperature (the soluble  
amount being calculated from the average composition of  
oxides contained in a thin steel sheet) and

(b) the number of rust spots formed on the thin steel  
sheet during a standard indoor exposure test to determine  
the extent of formation of rust. The test period was two  
weeks; the average temperature was 18°C; the average  
humidity was 62%; and

Fig. 4 is a graph showing the relationship between  
(a) the equilibrium S soluble amount (%S inc.) of  
oxides and

(b) the CaO concentration of the oxides.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following detailed description explains the  
Examples and results of the experiments performed. The  
Examples are not intended to limit or define the scope of  
the invention, which is defined in the appended claims.

A high frequency melting furnace filled with an Ar  
atmosphere was used to carry out the Si-deoxidation  
treatment (Si: 0.01 to 2.0 wt%) to treat an amount of an  
extremely low carbon steel having the following  
composition: C: 0.0015 to 0.0025 wt%; Mn: 0.15 to 0.22

wt%; P: 0.008 to 0.015 wt%; S: 0.002 to 0.020 wt%. This was followed by Al-deoxidation treatment or Ti-oxidation treatment or Al-Ti deoxidation treatment. Afterwards, Ca was added (Fe-Ca, CaSi, wherein the amount of Ca was 0.0005 to 0.0040 wt%). The composition of the oxides was altered and controlled to convert the oxides from  $\text{Al}_2\text{O}_3$ , Ti oxide,  $\text{Al}_2\text{O}_3$ -Ti oxide, or  $\text{SiO}_2$ -containing oxide to CaO-containing oxides.

Accordingly, the ingredients Al, Ti, Si, and Ca were reacted so as to alter the compositions of the oxides contained in the steel.

The molten steel was then cast, whereas the organization and characteristics of the inclusions contained in steel blocks, and having a particle diameter of 2  $\mu\text{m}$  or larger, were measured by the known method referred to as "EPMA". EPA means "Electron probe microanalyzer." In the EPMA method of analyzing a composition in a microscopic area, accurately, an electron beam is irradiated at an oxide inclusion, and characteristic X-rays are generated from elements in the oxide inclusion. Then the wave length and intensity of each of the X-rays are measured and analyzed with an X-ray spectroscope. Two distinct sets of analyzed results are obtained:

(i) Distribution of each of the elements by area-

analysis, as shown in Fig. 1.

(ii) Quantitative value of each oxide inclusion.

Especially,  $\Lambda$ , the optical basicity of the oxide inclusions in formula (ii) is calculated by using the quantitative value.

Furthermore, the steel block was rolled and a test piece was cut from the steel sheet formed by rolling the steel block. The test piece was then subjected to an exposure test for 24 hours in an experimental apparatus including a chamber having a constant temperature and a constant humidity (temperature: 60°C, humidity: 95%). Moreover, the organization and characteristics of the inclusions contained in the test piece treated in the above exposure test were also measured by EPMA, thereby determining the relationship between the compositions of the oxides and the probability of rust formation.

Fig. 1 of the drawings indicates the EPMA measurement results of inclusions present in the steel blocks.

As shown in Fig. 1, by observing the left-hand two columns, the presence of a  $\text{CaO-Al}_2\text{O}_3$  inclusion had the formula  $(47\text{wt}\%\text{CaO}-51\text{wt}\%\text{Al}_2\text{O}_3-2\text{wt}\%\text{Ti}_2\text{O}_3)$ . It had a low melting point but a high CaO concentration. It can be seen from the formulation that considerable CaS has been precipitated inside the inclusion and in areas around the inclusion.

In contrast, by observing the right-hand two columns of Fig. 1, there is noted a  $\text{CaO-Ti}_2\text{O}_3\text{-Al}_2\text{O}_3$  inclusion (23wt% $\text{CaO}$ -28wt% $\text{Al}_2\text{O}_3$ -47wt% $\text{Ti}_2\text{O}_3$ ) having a low  $\text{CaO}$  concentration. In this case almost no  $\text{CaS}$  was precipitated inside the inclusion or in areas around the inclusion.

Furthermore, it has been clearly found that in a thin steel sheet made from a steel block in which  $\text{CaS}$  has been precipitated together with oxides, a large amount of rust forms. Points at which oxides exist have become rust points, with the points at which oxides exist acting as the rust starting points.

Furthermore, the compositions of many other steel blocks were investigated, and research was repeatedly conducted on the compositions of the oxides, the precipitation conditions of the  $\text{CaS}$ , and the rust formation conditions, thereby clearly demonstrating the discovery that a higher  $\text{CaO}$  concentration, i.e., a higher optical basicity of oxides, causes easier precipitation of  $\text{CaS}$  in the areas around the oxides, hence readily forming starting points which will later become points at which rust forms. In Fig. 1, 47%  $\text{CaO}$  resulted in 3%  $\text{CaS}$ , while 23%  $\text{CaO}$  resulted in only 1%  $\text{CaS}$ .

Moreover, as a result of repeated research, it has been clearly found that the resulting amount of  $\text{CaS}$  and

the amount of rust formed will be further increased if the oxides have a higher sulfide capacity and if the molten steel has a reduced oxygen activity at the casting temperature of the continuous casting process.

5           Accordingly, as an important index, we have investigated the equilibrium S soluble amount (%S inc.) by considering both the optical basicity of the oxides and the oxygen activity during the casting process, the oxygen activity being calculated from the Al or Ti concentration.

Specifically, the equilibrium S soluble amount (%S inc.) in the steel is the soluble amount of the oxides at the casting temperature, as calculated by the method of D. J. Sosinsky, et al., in accordance with the equation (1) which follows hereinafter. The reference is D. J. Sosinsky and I. D. Sommerville, Met. Trans. B., 1986, Vol. 17B, pp. 331 - 337, the disclosure of which is incorporated by reference herein. As a result, it was clearly found that a larger value of the equilibrium S soluble amount (%S inc.) causes more CaS to form and deposit in areas located around the oxide particles.

20           However, in the equation (1) which follows, the value of the optical basicity A of each oxide was established by considering the coefficient of each oxide, from the compositions of the oxides, in accordance with the equation (2) which follows. The coefficients of various

25

oxides can be obtained by the method of J. A. Duffy (J. A. Duffy and M.D. Ingram, J. Inor. Nuclear Chem., 1975, Vol. 37, pp, 1203 - 1206). The equations are:

$$\log (\%S \text{ inc.}) = (21920 - 54640\Lambda)/T + 43.6\Lambda - 23.9 - \log [aO] + \log [\text{wt}\%S] \quad \dots \text{ (Equation 1)}$$

wherein

T represents the casting temperature (K) during the continuous casting process,

[wt%S] represents the concentration of S in the steel, and

[aO] represents the oxygen activity of the molten steel at the casting temperature (T) during the continuous casting process.

During Al-deoxidation, the log aO is expressed as follows:

$$\log aO = (-64000/T + 20.57 - 2\log[\text{wt}\%Al] - 0.086[\text{wt}\%Al] - 0.102 [\text{wt}\%Si])/3.$$

During Ti-deoxidation, the log aO is expressed as follows:

$$\log aO = (-60709/T + 20.97 - 2\log[\text{wt}\%Ti] - 0.084[\text{wt}\%Ti])/3.$$

However, when both Al and Ti are present, a smaller aO value should be applied, as follows:

$$\Lambda = 1.0 X(\text{CaO}) + 0.605 X(\text{Al}_2\text{O}_3) + 0.601 X(\text{TiO}_2) + 0.78 X(\text{MgO}) + 0.48 X(\text{SiO}_2) + 0.55 X(\text{Cr}_2\text{O}_3)$$

$$+ 0.59 X(\text{MnO}), \quad \text{--- (2)}$$

wherein

$\Lambda$  represents the optical basicity of the oxide inclusions

5  $X(\text{MmOn})$  represents the cation equivalent of the oxide, and

$$X(\text{MmOn}) = n \times N(\text{MmOn}) / \sum (n \times N(\text{MmOn})) \quad \text{--- (3)}$$

wherein

$N(\text{MmOn})$  represents the mol fraction of the oxide, and

$n$  represents the valence of oxygen contained in the oxide.

However, most of the Ti oxides present in the inclusions are present in the form of  $\text{Ti}_2\text{O}_3$ , as shown in the above-identified results of the EPMA measurements. On the other hand, when the optical basicity  $\Lambda$  is to be determined in accordance with the equation (2), it is also allowable that  $\text{Ti}_2\text{O}_3$  be converted to  $\text{TiO}_2$  so as to calculate  $X(\text{TiO}_2)$ .

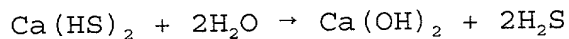
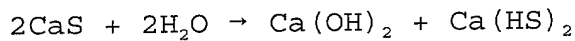
20 Next, as shown by the graph comprising Fig. 2, it is there shown that a relationship exists between (a) the equilibrium S soluble amount (%S inc.) (calculated in accordance with equations (1) and (2)) of the oxides at the casting temperature, and (b) the amount of rust  
25 formation in the areas around the oxides during the



standard rust formation tests. The tests were performed using an experimental apparatus including a chamber having a constant temperature and a constant humidity (temperature: 60°C, humidity: 95%).

5 As shown in the graph (Fig. 2), as the equilibrium S soluble amount (%S inc.) of the oxides increases, the amount of rust formation in the areas around the oxides also increases. In particular, the amount of rust formation suddenly and rapidly increases when the equilibrium S soluble amount (%S inc.) exceeds about 0.03 wt%.

10 In the areas around the inclusions having an equilibrium S soluble amount (%S inc.) (before the rust formation test) which is higher than about 0.03 wt%, CaS forms at an extremely high rate. The reason for this may be explained. The CaS, formed in the areas around the inclusions, is a hydrolyzable inclusion and is subjected to a hydrolysis reaction in a manner shown in the following chemical reactions (Iron & Steel, 1982, No. 13, 15 p. 301).



20 Furthermore, the corrosion of steel has also been found to be accelerated by dissociation of the resulting H<sub>2</sub>S.

The graph Fig. 3 shows a relationship between (a) the equilibrium S soluble amount (%S inc.) of the oxides at a certain casting temperature (the soluble amount being calculated from the average oxide composition of a thin steel sheet prepared for test use) and (b) the number of rust formation points in the thin steel sheet during an indoor exposure test for determining the amount of rust formation (test period: two weeks; average temperature: 18°C; average humidity: 62%).

As shown in the Fig. 3 graph, as the equilibrium S soluble amount (%S inc.) of the oxides increases, the number of rust points in a steel sheet also increases. In particular, the number of rust points suddenly and rapidly increases when the equilibrium S soluble amount (%S inc.) exceeds about 0.03 wt%.

Accordingly, it will be understood that the amount of rust formation in a steel product greatly depends upon the formation of CaS in the areas around the inclusions. The formation of CaS can be evaluated in accordance with the composition of the oxide inclusions, and the equilibrium S soluble amount (calculated from the temperature of the casting process and the oxygen activity of a molten steel) of the oxides at the casting temperature. Furthermore, it has been discovered from many experiments that once the equilibrium S soluble amount exceeds about 0.03 wt%, the

amount of CaS formed increases, resulting in a sudden increase in the amount of rust formed.

The present invention is beneficial for use in treating all kinds of Ca-containing steels obtained by adding Ca (usually in the form of a Ca alloy) to the molten steel. In particular, the present invention is suitable for use in treating any common steel such as high carbon steel, low carbon steel, and extremely low carbon steel; stainless steel such as a ferrite stainless steel, martensite stainless steel, and austenite stainless steel; and steel containing an oxide inclusion having a CaO content of 2  $\mu\text{m}$  or more.

The term "Ca-containing steel" herein means a steel whose Ca concentration is 0.0005 wt% or more.

With regard to the above-defined Ca-containing steel, an oxide that comprises  $\text{CaO-Al}_2\text{O}_3$  as its main component is present in an Al-deoxidized steel. An oxide that comprises CaO-Ti oxide as its main component exists in a Ti-deoxidized steel. An oxide that comprises  $\text{CaO-Al}_2\text{O}_3$ -Ti oxide as its main component is present in an Al/Ti-deoxidized steel.

Furthermore, we have found that a low Al steel and a low Ti steel, each of which is an Si-deoxidized steel, also contains an oxide  $\text{SiO}_2$ , a high Mn steel contains an oxide MnO; a high Cr steel such as stainless steel

contains an oxide  $\text{Cr}_2\text{O}_3$ ; and an Mn-containing steel contains an Mn-oxide. However, the present invention is suitable for treating even a complex oxide containing any combination of the above oxides. Moreover, the present invention is also suitable for use in treating steel containing as much as 5 wt% of other oxides.

In addition, the present invention is particularly beneficial for use in treating an oxide inclusion having a particle diameter of 2  $\mu\text{m}$  or larger, since fine particles having a particle diameter of less than 2  $\mu\text{m}$  are not likely to become starting points for development of rust. Here, the particle diameter is the average diameter obtained by averaging the diameters in both the rolling direction and the width direction of the sheet.

However, not all the oxide inclusions having a particle diameter of 2  $\mu\text{m}$  or larger need necessarily to be within the above described composition ranges. It is only required that at least about 80% of the above oxide particles be within the above described appropriate ranges.

The present invention is characterized in that the composition of the inclusions and the S concentration of steel are controlled so that the equilibrium S soluble amount (%S inc.) of oxides, when calculated in the above equation (1) will become about 0.03 wt% or less. On the

other hand, the composition of oxides can also be controlled by using a selected deoxidant and controlling the amount of its addition.

Fig. 4 is a graph showing the relationship between the equilibrium S soluble amount (%S inc.) of oxides and their CaO concentration, in relation to rust formation.

As shown in Fig. 4, the relationship between equilibrium S soluble amount (%S inc.) of oxides and their CaO concentration changes to some extent, depending upon the S concentration in the steel and the kind of deoxidation means that is present. However, if the CaO concentrations of the oxides are controlled so that the equilibrium S soluble amount (%S inc.) becomes about 0.03 wt% or less, it is still possible to effectively control the formation of rust on the steel surface.

On the other hand, in order to prevent the formation of large cluster-like inclusions and to prevent nozzle clogging during continuous casting, it is necessary that the oxide inclusions all have low melting points. In particular, the melting points of most oxide inclusions must be about 1650°C or less. For this reason, in order to prevent the formation of the large cluster-like inclusions and nozzle clogging during the casting process and to inhibit rust formation on the surface of steel products, it is important to appropriately select the

composition of oxides and S concentration of steel.

Furthermore, the casting temperature in the continuous casting process is typically controlled to a value about 10 to 80 degrees higher than the solidifying temperature of the steel.

#### Example 1

After removal of a molten steel from a converter, 300 tons of the molten steel were subjected to decarburization in an RH vacuum degassing apparatus. The amount of remaining C was adjusted to 0.0020 wt%. Mn was adjusted to 0.20 wt%, P was adjusted to 0.015 wt%, and S was adjusted to 0.010 wt%. The temperature was adjusted to 1600°C. Then, Al was added in an amount of 0.5 kg/ton to the molten steel, thereby reducing the dissolved oxygen content of the molten steel to 150 ppm.

Next, 70 wt% Ti-Fe alloy was added in an amount of 1.2 kg/ton to the molten steel, followed by deoxidation. Subsequently, an alloy wire containing 30 wt% of Ca and 60 wt% of Si was added in an amount of 0.3kg/ton into the molten steel, thereby adjusting the composition of the steel. After completion of the above steps, the Ti concentration was measured and determined to be 0.050 wt%. The Al concentration was measured as 0.002 wt% and the Ca concentration was measured as 15 ppm.

Next, casting was carried out in a two-strand

continuous slab casting equipment. At this time, the composition of the molten steel in the tundish was such that the Ti concentration was 0.050 wt%, the Al concentration was 0.002 wt%, the Ca concentration was 15 ppm, and the S concentration was 0.010 wt%, and the casting temperature was 1560°C. As a result, substantially nothing was found to have adhered to the immersion nozzle after 5 charges of continuous casting (without blowing any Ar gas).

Subsequently, a steel slab having a thickness of 220 mm was hot rolled until its thickness became 3.5 mm. Then, the steel slab was cold rolled to a thickness of 0.8 mm, followed by an annealing treatment at a temperature of 780°C for 45 seconds.

The final products were steel coils having a composition of Ti concentration 0.040 wt%, Al concentration 0.001 wt%, Ca concentration 15 ppm, and S concentration 0.010 wt%. The average oxide composition of 30 coils was measured by EPMA, and the measurement results were as follows: CaO 20 wt%, Al<sub>2</sub>O<sub>3</sub> 20 wt%, and TiO<sub>2</sub> 60 wt%.

In this way, the oxygen activity of the molten steel at the casting temperature became  $[aO] = 0.00076$ , the optical basicity of the oxide inclusions became  $\Lambda = 0.634$ , and the S concentration in the steel became  $[wt\%S] = 0.010$

wt%. The equilibrium S soluble amount (%S inc.) of the oxides, in accordance with the aforementioned equation (1) was 0.0084 wt%.

The coils were subjected to an indoor exposure test for determining susceptibility to rust formation (test period: two weeks; average temperature: 20°C; average humidity: 65%). The number of rust points formed was counted, and it was found that there were 20 rust points/100 cm<sup>2</sup>, which is the same level as that of an Al-deoxidized steel that does not contain Ca.

#### Comparative Example 1

After removal of molten steel from a converter, 300 tons of the molten steel was subjected to a decarburization treatment in an RH vacuum degassing apparatus. C was adjusted to 0.020 wt%, Mn was adjusted to 0.20 wt%, P was adjusted to 0.015 wt%, and S was adjusted to 0.010 wt%. The temperature was adjusted to 1600°C. Then, Al was added in an amount of 1.5 kg/ton to the molten steel. Furthermore, an alloy containing 75 wt% of Ti and 25 wt% of Fe was added in an amount of 0.6 kg/ton, followed by deoxidation. Subsequently, an alloy wire containing 30 wt% of Ca and 60 wt% of Si was added in an amount of 0.4 kg/ton to the molten steel. After completion of the above treatment, the Ti concentration was 0.050 wt%, the Al concentration was 0.035 wt% and the



Ca concentration was 20 ppm.

Next, a casting process was conducted in a two-strand continuous slab casting apparatus. At this time, the inclusions in the tundish were examined and were found to be spherical inclusions having a composition represented by the formula  $2\text{wt}\%\text{Ti}_2\text{O}_3\text{-}52\text{wt}\%\text{CaO-}46\text{wt}\%\text{Al}_2\text{O}_3$ .

Further, the composition of the molten steel within the tundish was investigated and it was found that its Ti concentration was 0.050 wt%, its Al concentration was 0.030 wt%, its Ca concentration was 25 ppm, and its S concentration was 0.010 wt%. The casting temperature was  $1560^\circ\text{C}$ . As a result, essentially nothing was found to have adhered to the immersion nozzle after 5 charges of continuous casting (without blowing any Ar gas).

Subsequently, a steel slab was hot rolled until its thickness was 3.5 mm. Then, the steel slab was cold rolled to a thickness of 0.8 mm, followed by annealing at a temperature of  $780^\circ\text{C}$  for 45 seconds.

The final products were steel coils having a Ti concentration of 0.040 wt%, an Al concentration of 0.030 wt%, a Ca concentration of 20 ppm, and an S concentration of 0.010 wt%. The average oxide composition of 30 coils, measured by EPMA, was CaO 50 wt%,  $\text{Al}_2\text{O}_3$  48 wt%, and  $\text{TiO}_2$  2 wt%.

The oxygen activity of the molten steel at the

casting temperature was  $[aO] = 0.00076$ , the optical basicity of the oxide inclusions was  $\Lambda = 0.6667$ , and the S concentration in steel was  $[wt\%S] = 0.010$  wt%. The equilibrium S soluble amount (%S inc.) of the oxides, in accordance with the aforementioned equation (1), was 0.106 wt%.

The coils were subjected to an indoor exposure test to determine the amount of rust formation (testing period: two weeks; average temperature: 20°C; average humidity: 65%). When the number of rust points formed was counted, it was found that there were 252 rust points/100 cm<sup>2</sup>, indicating that the rust points were substantially more numerous than those of an Al-deoxidized steel not containing Ca, and also more numerous than those of Example 1.

In this way, with the benefit of the present invention, it is possible to effectively inhibit the rust formation which would otherwise be caused due to the oxide inclusions, thereby solving a problem which has long been of concern in Ca-containing steels.

- 25 -

WHAT IS CLAIMED IS:

4. A Ca-containing rust-resistant steel having controlled amounts of inclusions and S concentration, said Ca-containing steel comprising Ca at a concentration of 0.0005 wt% or more, characterized in that the composition of said inclusions and said S concentration in said steel are so controlled that the equilibrium S soluble amount (%S inc.) of CaO-containing oxide inclusions contained in said Ca-containing steel is about 0.03 wt% or less.

2. A Ca-containing rust-resistant steel according to claim 1, wherein the equilibrium S soluble amount (%S inc.) of at least 80% of said oxide inclusion particles, having a particle diameter of 2  $\mu$ m or larger, is about 0.03 wt% or less.

3. A Ca-containing rust-resistant steel according to claim 1, wherein said equilibrium S soluble amount (%S inc.) value is determined in accordance with the following equation (1), including as its parameters the inclusions optical basicity calculated from the composition of said oxide inclusions, the casting temperature and the components forming the steel, such equation being

$$\log (\%S \text{ inc.}) = (21920 - 54640\Lambda)/T$$

$$+ 43.6\Lambda - 23.9 - \log [aO] + \log [wt\%S], \quad \dots (1)$$

10        wherein

T represents the casting temperature (K) during the continuous casting process,

[wt%S] represents the concentration of S contained in said steel,

15        [aO] represents the oxygen activity of said molten steel at said casting temperature (T) during a continuous casting process, and wherein during Al-deoxidation,

$$\log aO = (-64000/T + 20.57 - 2\log[wt\%Al] - 0.086[wt\%Al] - 0.102 [wt\%Si]/3,$$

20        and wherein during Ti-deoxidation,

$$\log aO = (-60709/T + 20.97 - 2\log[wt\%Ti] - 0.084[wt\%Ti]/3,$$

25        and provided that, when Al and Ti are present in said steel a reduced aO oxygen activity is provided according to the following equation (2):

$$\begin{aligned} \Lambda = & 1.0 X(CaO) + 0.605 X(Al_2O_3) + 0.601 X(TiO_2) \\ & + 0.78 X(MgO) + 0.48 X(SiO_2) + 0.55 X(Cr_2O_3) \\ & + 0.59 X(MnO) \quad \dots (2) \end{aligned}$$

wherein

30         $\Lambda$  represents the optical basicity of oxide inclusions, and

X (MmOn) represents the cation equivalent of the oxide present, according to the following equation (3):

$$X(\text{MmOn}) = n \times N(\text{MmOn}) / \sum (n \times N(\text{MmOn})), \quad \dots (3)$$

35 wherein

$N(\text{MmOn})$  represents the mol fraction of oxide present and

$n$  represents the valence of oxygen contained in said oxide.

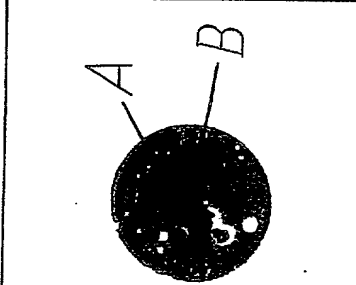
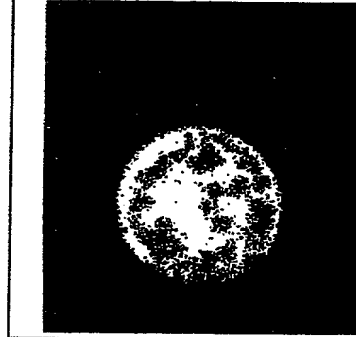
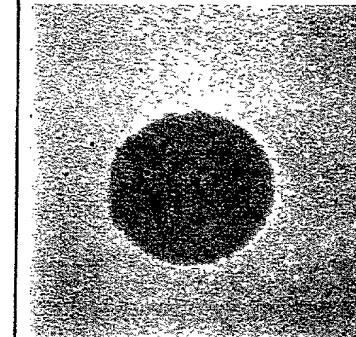
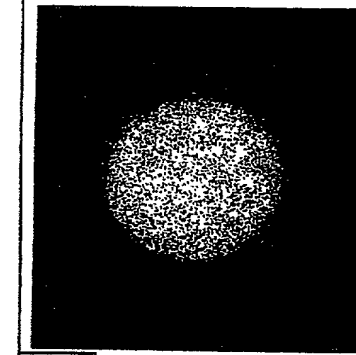
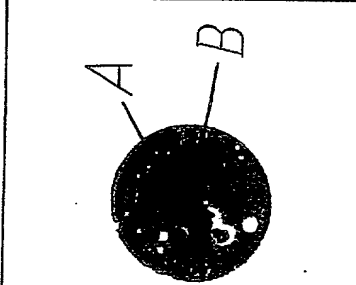
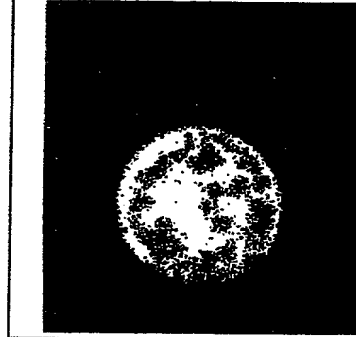
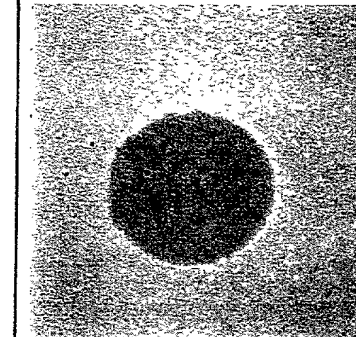
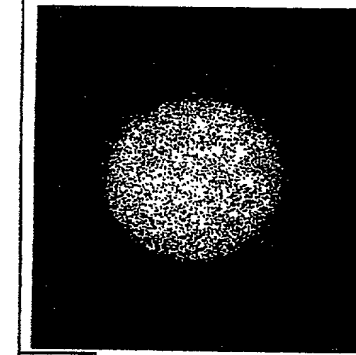
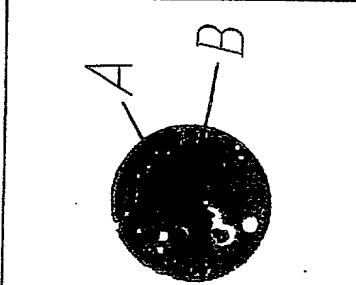
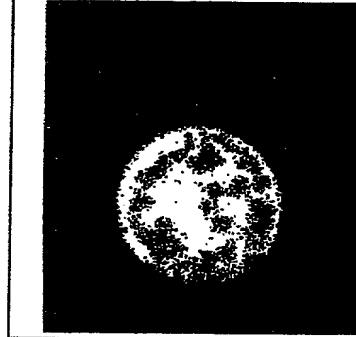
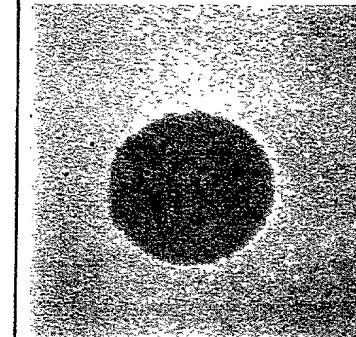
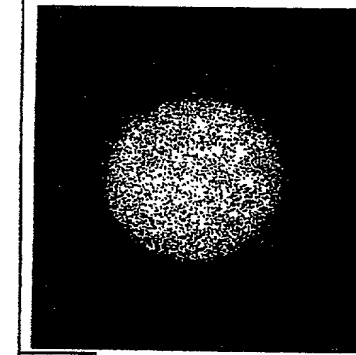
4. A method for manufacturing a Ca-containing rust-resistant steel, said steel containing Ca at a concentration of about 5 ppm or more, comprising performing a refining process for refining said steel, wherein the composition of inclusions and the S concentration of steel are so controlled that the equilibrium S soluble amount (%S inc.) of CaO-containing oxide inclusions present in said Ca-containing steel is about 0.03 wt% or less.

10

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SE	AI	SE	AI
			
Ti	Ca	Ti	Ca
			
O	S	O	S
			
47%CaO—51%Al <sub>2</sub> O <sub>3</sub> —2%Ti <sub>2</sub> O <sub>3</sub> — 3%CaS 100%CaS		23%CaO—28%Al <sub>2</sub> O <sub>3</sub> —47%Ti <sub>2</sub> O <sub>3</sub> —1%CaS	
AI DEOXIDATION - Ca TREATMENT 20 μm		Ti DEOXIDATION - Ca TREATMENT 5 μm	

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FIG. 2

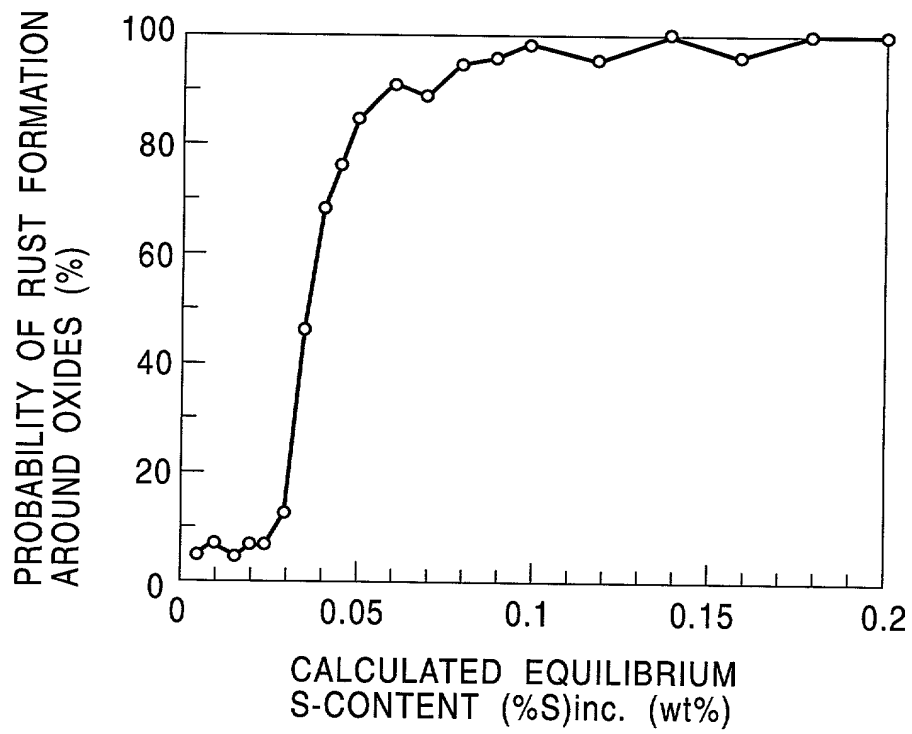




FIG. 3

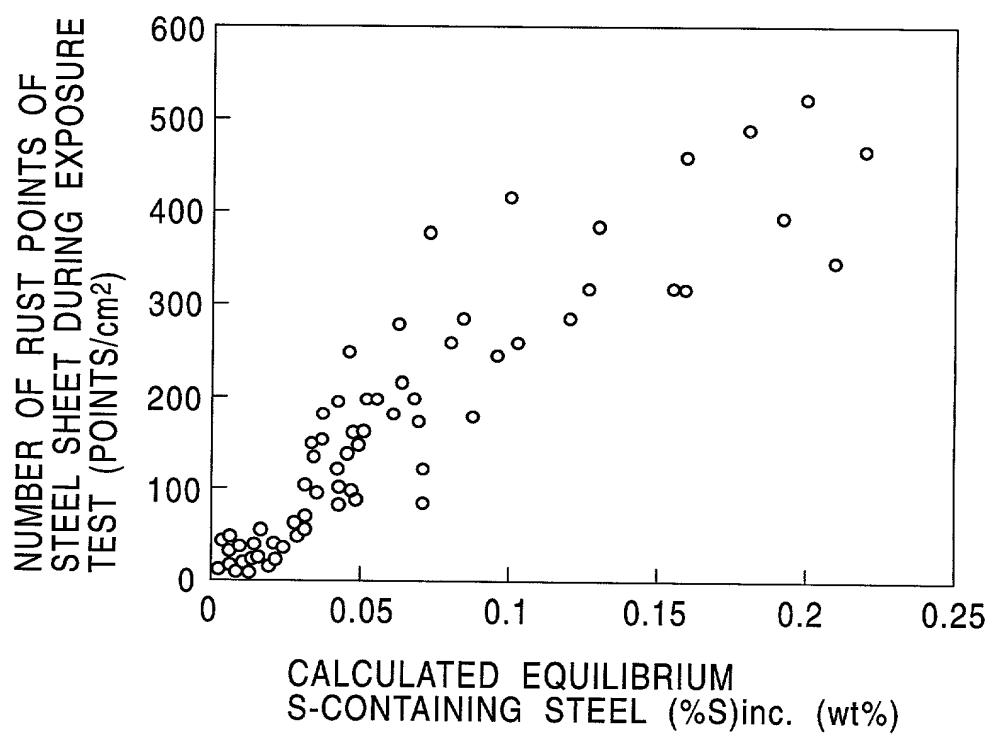
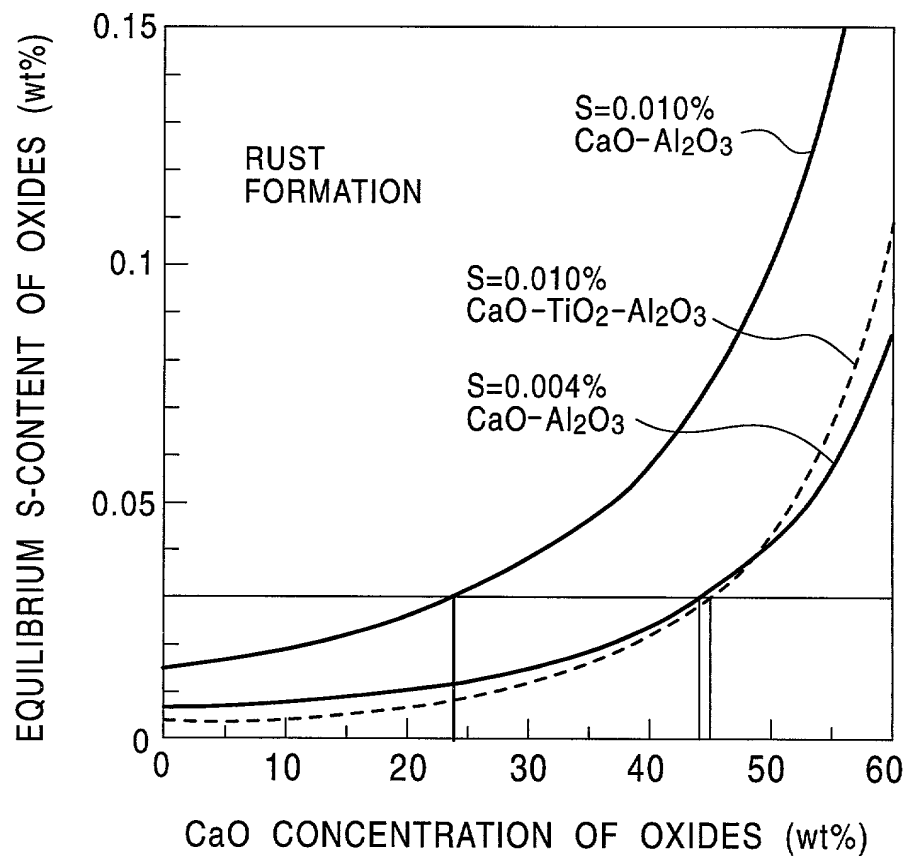


FIG. 4



Express Mail Label EL618696194US

- ☒ Original Application
- ☐ PCT National Application  
U.S. Designated Office
- ☐ Continuation or Divisional Application
- ☐ Continuation-in-Part Application

**COMBINED DECLARATION,  
POWER OF ATTORNEY AND PETITION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled RUST-RESISTANT CALCIUM STEEL

☐ which is described in the specification and claims

☒ attached hereto.

☐ filed on \_\_\_\_\_

Application Serial No. \_\_\_\_\_

and was amended on \_\_\_\_\_

*(if applicable)*

☐ which is described in International Application No. \_\_\_\_\_

filed \_\_\_\_\_ and as amended on \_\_\_\_\_

*(if any),*

which I have reviewed and for which I solicit a United States patent.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe that this invention was ever known or used in the United States before my or our invention thereof or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application or said international application, or in public use or on sale in the United States of America more than one year prior to this application or said international application, or that the invention has been patented or made the subject of an inventor's certificate issued before the date of this application or said international application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months prior to this application or said international application, or that any application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application or said international application by me or my legal representatives or assigns except as identified below.

2025 OCT 22 09:55:56

COMBINED DECLARATION, POWER OF ATTORNEY AND PETITION  
(Page 2)

Attorney Docket No. 1396-00

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International Application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application(s) for patent or inventor's certificate or of any PCT International Application having a filing date before that of the application on which priority is claimed:

Number	Country	Date of Filing (day, month, year)	Priority Claimed
11-285471	Japan	06, 10, 1999	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no
			<input type="checkbox"/> yes <input type="checkbox"/> no
			<input type="checkbox"/> yes <input type="checkbox"/> no
			<input type="checkbox"/> yes <input type="checkbox"/> no
			<input type="checkbox"/> yes <input type="checkbox"/> no

I hereby claim the benefit under Title 35, United States Code, §119(e) or §120 (as applicable) of any United States application(s) or §365(c) of any PCT International Application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International Application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112:

(Application Serial No.)

(Filing Date)

(Status) (patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status) (patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the registered attorneys listed under Customer No. 022469 and the following registered attorneys to prosecute this application and transact all business in the United States Patent and Trademark Office connected therewith:

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**COMBINED DECLARATION, POWER OF ATTORNEY AND PETITION**  
(Page 3)

Attorney Docket No. 1396-00

I hereby petition for grant of a United States Letters Patent on this invention.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1. FULL NAME OF SOLE OR FIRST INVENTOR <b>Seiji Nabeshima</b>		INVENTOR'S SIGNATURE <i>Seiji Nabeshima</i>	DATE Sep. 14, 2000
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4. FULL NAME OF ADDITIONAL JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
5. FULL NAME OF ADDITIONAL JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
6. FULL NAME OF ADDITIONAL JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
7. FULL NAME OF ADDITIONAL JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			